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Article

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Ruthenium(II)-Catalyzed Direct Addition of Indole/Pyrrole C2-H Bonds to Alkynes

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ABSTRACT: A ruthenium-catalyzed C2-hydroindolation of alkynes has been achieved. This protocol provides a rapid and concise access to kinds of 2-alkenyl substituted *N*-(2-pyridyl)indoles in which the pyridyl moiety can be easily removed to afford free (N-H) indoles under mild conditions. Various arenes and alkynes including electron-deficient and electron-rich internal alkynes and terminal alkynes allow for this transformation.

INTRODUCTION

Transition-metal catalyzed addition of aryl C-H bonds to alkynes belongs to a synthetically important C-C bond forming reaction,[1] as this approach provides an atom- and step -economic strategy for constructing various alkenyl aromatic compounds directly from inactivated simple arenes instead of the conventional aryl halides or arylmetallic reagents.[2] Of these processes, hydroarylation of alkynes through chelation assistance has lately attracted increasing interest because it allows site-selectively installing alkenyl group into aromatic molecules.[3] For example, Ackermann,[4] Chang,[5] Yoshikai[6] and Hiyama/Nakao[7] groups, *etc*., have revealed that transition-metal catalysts could effectively enhance addition of phenyl C-H[4-6] or pyridine C-H[7] bonds to alkynes with the aid of heteroatom-containing groups, but there are rare reported cases involved in hydroindolation of alkynes *via* C-H functionalization,[3a, 3d] despite alkenyl-substituted indole nucleus can be found in natural products and complex biologically active molecules.[8]

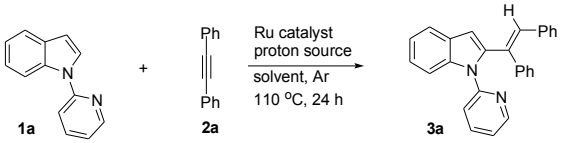
Remarkably, comparison with C2- position of indole, C3-position is an inherently nucleophilic reactive site, therefore Lewis acids could easily realize the additions of indole C3-H bonds to alkynes *via* Friedel-Craft–type process.[9] Nevertheless, heteroatom directed *ortho*-metelation reaction provides concise access to site-selective indole C2-H functionalization,[10] but there are very rare examples about C2-hydroindolation of alkynes. To date, the pioneering reports by Schipper, Yoshikai and

Kanai group described that Rh(III) (5 mol %) catalysts,[11] Co(II) (10 mol %)/Grignard reagent (0.60 equiv) catalytical system[12] or Co(III) (5 mol %) catalyst[13] could enable effective intermolecular C2-hydroindolation of alkynes, in which *N*, *N*-dimethylcarbonyl or pyrimidyl group was employed as a directing group, respectively. Unfortunately, these protocols only allow the use of electron-rich internal alkynes or aryl substituted terminal alkynes. Herein we demonstrated a valuable complementary approach to C2-hydroindolation of alkynes using ruthenium salts as catalyst, and the substrate scope could be further extended to electron-poor internal alkynes and acyl- or alkyl-substituted terminal alkynes.

RESULTS AND DISCUSSION

Initially, we investigated the effect of various Ru catalyst (5 mol %) on the addition of *N*-(2-pyridyl)indole (**1a**) C2-H to diphenylacetylene (**2a**) in the presence of $AgSbF_6$ (20 mol %) and PivOH (1.0 equiv) using 1, 4-dioxane as solvent at 110 ^oC for 24 h (Table 1, entries 1-5), and we soon found the dimeric species $[RuCl_2(p\text{-cymene})]_2$ provided 54% yield of the desired alkenylation product **3a**, whose structure was already unambiguously assigned by its single crystal X-ray analysis [see Supporting Information (SI) for more details] (compare entries 1-4 with 5). Subsequently, further improvement of the reaction (83% yield of **3a**) was achieved when $AgBF_4$ and AcOH was employed as an additive and a proton source, respectively (compare entries 5-9 with 10). It is worth noting that only trace of **3a** could be observed in the absence of $AgBF_4$ (compare entry 10 with 11).[14] To our delight, after various solvents including toluene, acetonitrile and 1, 2-dichloroethane (DCE) were evaluated for this transformation, the yield of product **3a** was significantly increased to 97% using 7 mol % of $[RuCl_2(p\text{-cymene})]_2$ in toluene (compare entries 10, 12 with 13). Most importantly, the similar yield (98% yield of **3a**) could also be obtained in DMF solvent system even no silver salt additives were employed (compare entry 13 with 14). By the way, when DMF was used as solvent and the spots on the TLC plate of the reaction mixture looks very clean. On the contrary, alternative solvents afforded poorer results in the absence of silver additives (entries 15 and 16).

Table 1. Optimization of the Reaction Parameters [a]



entry	Ru salts (5 mol %)	additive (20 mol %)	solvent	proton source	yield (%) [b]
1	$RuCl_3$	$AgSbF_6$	1, 4-dioxane	PivOH	nr [c]
2	$Ru_3(CO)_{12}$	$AgSbF_6$	1, 4-dioxane	PivOH	trace
3	**A** [d]	$AgSbF_6$	1, 4-dioxane	PivOH	nr [c]
4	**B** [e]	$AgSbF_6$	1, 4-dioxane	PivOH	nr [c]
5	**C** [f]	$AgSbF_6$	1, 4-dioxane	PivOH	54

6	**C**	AgOAc	1, 4-dioxane	PivOH	73
7	**C**	$AgPF_6$	1, 4-dioxane	PivOH	40
8	**C**	$AgBF_4$	1, 4-dioxane	PivOH	75
9	**C**	$AgBF_4$	1, 4-dioxane	*i*-PrOH	19
10	**C**	$AgBF_4$	1, 4-dioxane	AcOH	83
11	**C**	—	1, 4-dioxane	AcOH	trace
12	**C**	$AgBF_4$	1, 4-dioxane	AcOH	94 [g]
13	**C**	$AgBF_4$	toluene	AcOH	97 [g]
14	C	—	DMF	AcOH	98 [g]
15	**C**	—	CH_3CN	AcOH	73 [g]
16	**C**	—	DCE	AcOH	62 [g, h]

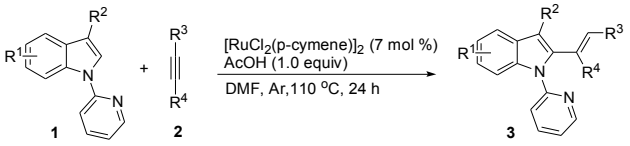
[a] Unless otherwise noted, all the reactions were carried out using *N*-(2-pyridyl)indole (**1a**) (0.10 mmol) and alkyne (**2a**) (0.10 mmol) with Ru catalyst (5 mol %) in the presence of additive (20 mol %) and proton source (1.0 equiv) in 1, 4-dioxane (2.0 mL) at 110 °C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b] Isolated yield. [c] nr = no reaction. [d] **A** = $RuH_2(CO)(PPh_3)_2$; [e] **B** = $RuHCl(CO)(PPh_3)_3$; [f] **C** = $[RuCl_2(p\text{-cymene})]_2$; [g] 7 mol % of catalyst **C** was used; [h] DCE = 1, 2-dichloroethane.

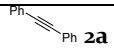
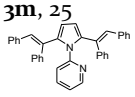
With an optimized catalytic system in hand, we first investigated the reactivity of various *N*-(2-pyridyl)indole derivatives. As shown in Table 2, all of 5- or 6- or 7- substituted indole substrates exhibited excellent reactivity with exclusive *E*-stereochemistry, no matter whether electronic-withdrawing (such as 5-CN, 5-NO_2, 5-CO_2Et, 5- halide, 6-halide, *etc*) or electron-donating groups (such as 5-MeO, and 7-Me, *etc*) are introduced to the benzene ring. For example, the C2-hydroindolation of diphenylacetylene (**2a**) with 5-ethoxycarbonyl-*N*-(2-pyridyl) indole (**1h**) and 7-methyl-*N*-(2-pyridyl)indole (**1k**) could afford the desired alkenylation product **3f** and **3k** in 91% and 94% yield, respectively (entries 8 and 11). On the contrary, the substituted group (R_2) at C3-position of indole showed significantly electronic effects, the substrate (**1l**) with electron-donating group (3-Me) on the indole ring produced 96% yield of **3l**. However, 3-acetyl-*N*-(2-pyridyl) indole (**1m**) underwent obviously worse conversion and provided lower yield of **3m** (25%, entries 12 and 13). Moreover, this reaction protocol could also smoothly convert *N*-(2-pyridyl)pyrrole (**1n**) to the corresponding 2, 5-bis-alkenylation pyrrole derivative **3n** (40% yield) and 2-alkenylation pyrrole product **3o** (52% yield) possibly due to a double migratory insertion of alkyne **2a** into Ru(II) intermediate (entries 14), respectively. For the *N*-(2-pyrimidyl)indole (**1o**), the desired 2-alkenylation derivatives **3p** could also be obtained in 83 % yield (entry 15).

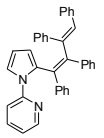
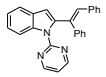
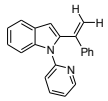
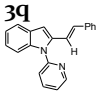
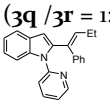
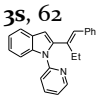
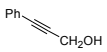
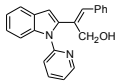
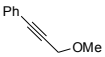
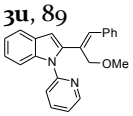
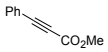
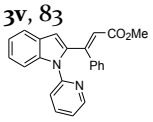
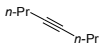
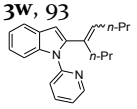
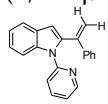
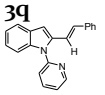
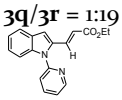
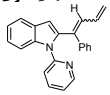
Subsequently, we further investigated the scope of the C2-hydroarylation of *N*-(2-pyridyl) indole (**1a**) by employing differently substituted alkynes. It was found that this transformation tolerated a variety of electron-rich internal alkynes, such as diarylacetylene (**2a**), aryl alkyl alkyne (**2c**), aryl hydroxymethyl alkyne (**2d**), aryl methoxylmethyl internal alkyne (**2e**), dialkyl alkyne

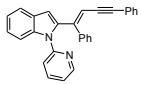
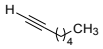
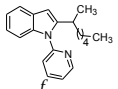
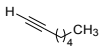
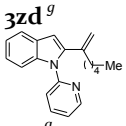
(**2g**), silyl-substituted alkyne (**2h**), aryl alkenyl alkyne (**2j**) and aryl alkynyl alkyne (**2k**), *etc*., could couple with **1a** in good to excellent yields (entries 17, 18, 19, 21, 22, 24 and 25). It is worth noting that unsymmetric internal alkyne **2c** gave two products **3s** and **3t** in around 2:1 ratio where the reaction was under steric control (entry 17). In contrast, aryl hydroxymethyl internal alkyne **2d** and aryl methoxylmethyl internal alkyne **2e** provided **3u** (89% yield) and **3v** (83% yield) with high regioselectivity probably due to the weak coordination between Ru(II) and ether or alcohol oxygen atom (entries 18 and 19). Importantly, this reaction protocol remarkably tolerated electron-poor internal aryl ethoxycarbonyl alkyne (**2f**), and gave the desired alkenylation product **3w** in 93% yield (entry 20). Moreover, electron-rich and electron-poor terminal alkynes (**2b** and **2i**) also allowed for this transformation, and afforded the corresponding 1,1-disubstituted alkene (**3q**) and 1, 2-disubstituted alkene **3y** (54% yield) with high regioselectivity (entries 16 and 23), which is different from the Ru-catalyzed alkenylation of *N*, *N*-dimethylbenzamide with terminal alkynes.[15] Surprisingly, when hept-1-yne (**2l**) was applied to this reaction system, the major product was the C2-alkylation compounds **3zb** and **3zc** (**3zb**/**3zc** = 6.7) which were possibly derived from the C2-alkenylation indole intermediates *via* a reduction process, in which DMF act as a reducing agent (entry 26).[16] On the contrary, employing toluene as solvent furnished the desired C2-alkenylation products **3zd** and **3ze** in the overall yield of 86% (entry 27).

Table 2. Ru(II)-Catalyzed Addition of Indole C2-H Bonds to Alkynes



entry	indole **1**	alkyne **2**	**3**, yield (%)[b]
1	**1a**, $R^1 = R^2 = H$	 **2a**	**3a**, 98
2	**1b**, R^1 = 5-MeO, $R^2 = H$	2a	**3b**, 97
3	**1c**, R^1 = 5-F, $R^2 = H$	2a	**3c**, 80
4	**1d**, R^1 = 5-Cl, $R^2 = H$	2a	**3d**, 94
5	**1e**, R^1 = 5-Br, $R^2 = H$	2a	**3e**, 95
6	**1f**, R^1 = 5-NO_2, $R^2 = H$	2a	**3f**, 74
7	**1g**, R^1 = 5-CN, $R^2 = H$	2a	**3g**, 94
8	**1h**, R^1 = 5-CO_2Me, $R^2 = H$	2a	**3h**, 91
9	**1i**, R^1 = 6-F, $R^2 = H$	2a	**3i**, 85
10	**1j**, R^1 = 6-Cl, $R^2 = H$	2a	**3j**, 86
11	**1k**, R^1 = 7-Me, $R^2 = H$	2a	**3k**, 94
12	**1l**, $R^1 = H$, R^2 = 3-Me	2a	**3l**, 96
13	**1m**, $R^1 = H$, R^2 = 3-Ac	2a	**3m**, 25
14		2a	 **3n**, 40

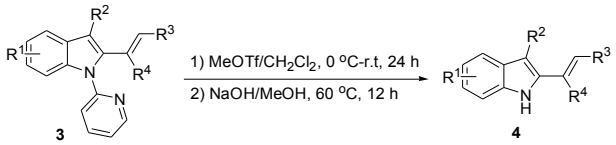
		1n		 **3o**, 52
15	 10		2a	 **3p**, 83
16	**1a**, $R^1 = R^2 = H$		 2b	 **3q**  **3r** **3q** + **3r** = 81 [c] (**3q** /**3r** = 1:4) [d]
17	**1a**, $R^1 = R^2 = H$		 2c	 **3s**, 62  **3t**, 34
18	**1a**, $R^1 = R^2 = H$		 **2d**	 **3u**, 89
19	**1a**, $R^1 = R^2 = H$		 **2e**	 **3v**, 83
20	**1a**, $R^1 = R^2 = H$		 **2f**	 **3w**, 93
21	**1a**, $R^1 = R^2 = H$		 **2g**	 **3x**, 95 (*E*/*Z* = 4.2:1) [e]
22	**1a**, $R^1 = R^2 = H$		 **2h**	 **3q**  **3r** **3q** + **3r** = 98 [c] **3q**/**3r** = 1:19 [d]
23	**1a**, $R^1 = R^2 = H$		 2i	 **3y**, 54
24	**1a**, $R_1 = R_2 = H$		 **2j**	 **3z**, 81 (*E*/*Z* = 6.7:1) [e]

25	**1a**, $R^1 = R^2 = H$	 **2k**	 **3za**, 88
26	**1a**, $R^1 = R^2 = H$	 **2l**	 **3zb** [f] **3zc** [f] **3zb** + **3zc** = 76 **3zb**/**3zc** = 6.7:1
27	**1a**, $R^1 = R^2 = H$	 **2l**	 **3zd** [g] **3ze** [g] **3zd** + **3ze** = 86 **3zd**/**3ze** = 2.3:1

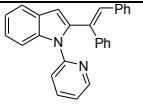
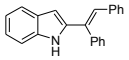
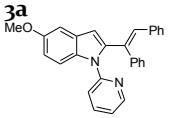
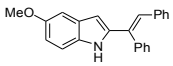
[a] Unless otherwise noted, all the reactions were carried out using *N*-substituted indole or pyrrole (**1**) (0.10 mmol) and alkyne (**2**) (0.20 mmol) with $[RuCl_2(p\text{-cymene})]_2$ catalyst (7 mol %) in the presence of AcOH (1.0 equiv) in DMF (2.0 mL) at 110 ˚C for 24 h under Ar in a sealed reaction tube, followed by flash chromatography on SiO_2. [b] Isolated yield. [c] the total isolated yield of mixture **3q** and **3r**. [d] The ratio of **3q**/**3**r was determined by ^{1}H NMR spectroscopy. [e] The ratio of *E*/*Z* was determined by ^{1}H NMR spectroscopy. [f] When PivOH was used as the source of H atoms, the overall yield of **3zb** and **3zc** would decrease to 56%. [g] The solvent (DMF) was changed to toluene.

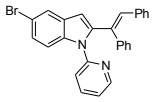
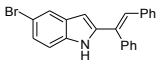
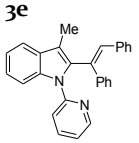
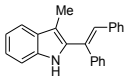
Finally, we easily removed the pyridyl group on the alkenylation product **3** under CH_3OTf/NaOH conditions to provide the corresponding free (N-H) indole derivative **4**, several examples were shown in Table 3 (see SI for more details), which could be used for further synthetic transformations. [12]

Table 3. Several Examples about the Removal of the Pyridine Directing Group [a]



3 **4**

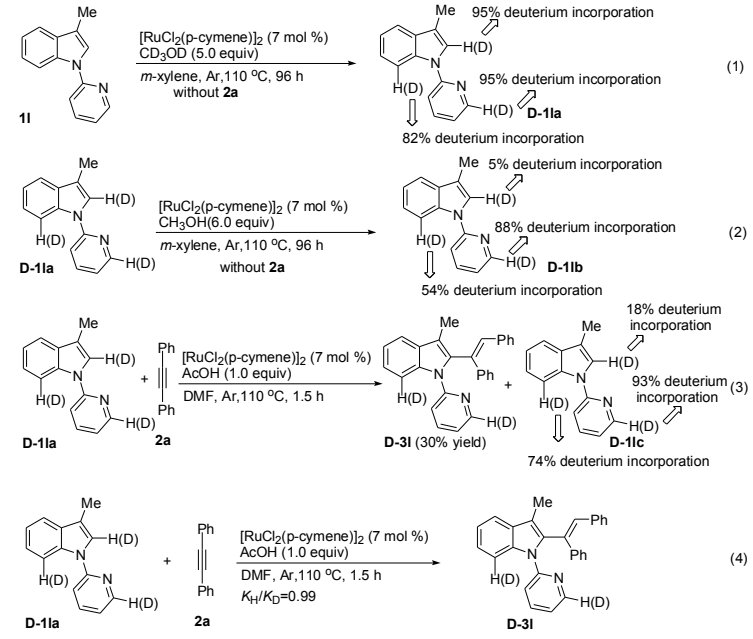
entry	*N*-(2-pyridyl)indole **3**	free (N-H) indole **4**	yield (%) [b]
1	 **3a**	 **4a**	90
2	 **3b**	 **4b**	82

3	 **3e**	 **4c**	86
4	 **3l**	 **4d**	86

[a] The CH_2Cl_2 (7.5 mL) solution of *N*-(2-pyridyl)indole **3** (0.3 mmol) with MeOTf (0.36 mmol) was stirred from 0 °C – r.t. for 24 h. After removal of the solvent, aqueous NaOH (2.0 M, 1.8 mL) and MeOH (3.6 mL) was added to the corresponding mixture, respectively, and then stirred at 60 ˚C for 12 h under Ar atmosphere, followed by flash chromatography on SiO_2. [b] Isolated yield.

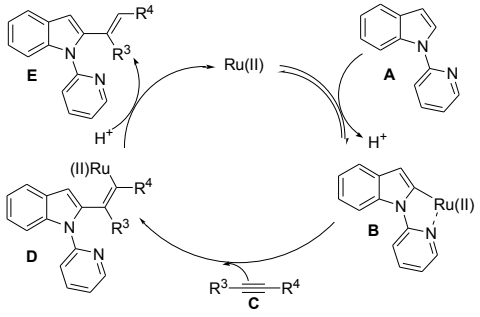
To further investigate the mechanism, the H/D exchange of 3-methyl-*N*-(2-pyridyl)indole **1l** was conducted in Ru(II)/CD_3OD system for 96 h in absence of alkyne **2a**, 95% deuterium incorporation at C2-position was observed (Scheme 1, Eq. 1). Notably, 82% (C7-position of indole) and 95% (C6-position of pyridine) deuterium incorporation was also observed (see SI for more details about its ^{1}H NMR spectra).[17, 18] On the other hand, the content of C2-deuterium in **D-1la** under Ru(II)/CH_3OH system[19] and Ru(II)/AcOH system could be decreased from 95% to 5% and 18%, respectively (Eq. 2 and Eq. 3) (See SI for more details about the corresponding ^{1}H NMR spectrum of **D-1la**, **D-1lb** and **D-1lc**). These results clearly demonstrate that the first step of a reversible Csp^2-H bond cleavage process was involved in the transformation. Subsequently, the intermolecular isotope effect (K_H/K_D = 0.99) further indicated that the reversible Csp^2-H bond breaking was not the rate-limiting step of the reaction (Eq. 4).

Scheme 1. Preliminary Mechanistic Studies



On the basis of the above observations, we proposed the possible mechanism as Scheme 2. The transformation is initiated by the coordination of the nitrogen atom from the pyridine ring to cationic ruthenium center, followed by an electrophilic substitution to produce the five-membered cycloruthenium complexes **B** with concomitant loss of a proton.[17b, 20] Of course, the possibility of OAc-assisted deprotonative cyclometalation pathway could also not be ruled out.[4, 21] Subsequently, alkynes (**C**) insertion into ruthenium-C2 (indole) bond would lead to alkenyl Ru intermediates **D**, which would be further protonated to afford alkenylation product **E** and regenerated the ruthenium catalyst.

Scheme 2. The Proposed Catalytic Cycle



In summary, we have developed the first ruthenium-catalyzed C2-hydroindolation of alkynes, which provides efficient access to various alkenylation indoles.[22] This new approach tolerates variety arenes and alkynes, especially for electron-poor internal alkynes and acyl- or alkyl-substituted terminal alkynes which have not been easily accessible through existing synthetic methods.[11-13] Moreover, the pyridyl moiety could also be easily removed to produce free (N-H) indoles that can be further broadly used in organic transformations.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Flash chromatography was performed on silica gel (40~63 mm) by standard technique. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using HPLC Mass Spectrometer. High resolution exact mass measurements (HR-MS) were performed on a TOF spectrometer. Infrared spectra (IR) were reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. Crystal data were obtained by

employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the ϕ-ω scan mode. The structure was solved by direct methods SHELXS-97. Indole substrates including 1-(pyridin-2-yl)-1H-indole (**1a**) , [23] 5-methoxy-1-(pyridin-2-yl)-1H-indole (**1b**), [23] 5-chloro-1-(pyridin-2-yl)-1H-indole (**1d**), [24] 5-bromo-1-(pyridin-2-yl)-1H-indole (**1e**), [23] *1*-(pyridin-2-yl)-1H-indole-5-carbonitrile (**1g**), [25] methyl 1-(pyridin-2-yl)-1H-indole-5-carboxylate (**1h**), [26] 7-methyl-1-(pyridin-2-yl)-1H-indole (**1k**), [27] 3-methyl-1-(pyridin-2-yl)-1H-indole (**1l**), [23] 1-(1-(pyridin-2-yl)-1H-indol-3-yl)ethanone (**1m**), [25] 2-(1H-pyrrol-1-yl)pyridine (**1n**), [28] and 1-(pyrimidin-2-yl)-1H-indole (**1o**) [23] were prepared using the previous reported procedure. All the alkyne substrates are commercially available.

Procedures for the preparation of indole substrates (1c, 1f, 1i and 1j)

Procedure A [23] (**Synthesis of 1c and 1f**): A mixture of indole starting material (5.0 mmol), 2-bromopyridine (6.0 mmol), KOH (0.70 g, 12.5 mmol) in DMSO (6 mL) was vigorously stirred at 120 ^{o}C under argon atmosphere for 30 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (40 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was extracted with EtOAc (3 × 30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuum*, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give the desired indole derivatives.

5-Fluoro-1-(pyridin-2-yl)-1H-indole (**1c**): light yellow solid; M. p. = 62–64 °C; 869 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56-8.55 (m, 1H), 8.23 (dd, *J* = 9.1 Hz, 4.6 Hz, 1H), 7.83-7.79 (m, 1H), 7.72 (d, *J* = 3.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 9.2 Hz, 2.6 Hz, 1H), 7.16 (ddd, *J* = 7.3 Hz, 4.9 Hz, 0.7 Hz, 1H), 7.02 (td, *J* = 9.1 Hz, 2.6 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.6 (d, *J* = 236.7 Hz), 152.4, 148.9, 138.5, 131.8, 131.0 (d, *J* = 10.1 Hz), 127.3, 120.2, 114.5 (d, *J* = 9.2 Hz), 114.1, 111.2 (d, *J* = 25.4 Hz), 106.0 (d, *J* = 23.4 Hz), 105.4 (d, *J* = 4.3 Hz). IR (KBr, cm $^{-1}$): 3057, 1589, 1474, 1343, 1264, 1208, 1145, 741. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}FN_2$ 213.0823, found 213.0825.

5-Nitro-1-(pyridin-2-yl)-1H-indole (**1f**): yellow solid; M. p. = 88–90 °C; 789 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63-8.61 (m, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.33 (d, *J* = 9.2 Hz, 1H), 8.18 (dd, *J* = 9.2 Hz, 2.3 Hz, 1H), 7.90 (td, *J* = 8.2 Hz, 1.9 Hz, 1H), 7.82 (d, *J* = 3.5 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.29 (ddd, *J* = 7.4 Hz, 4.9 Hz, 0.7 Hz, 1H), 6.88 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.7, 149.1, 142.6, 138.9, 138.0, 129.7, 129.0, 121.4, 118.4, 117.7, 114.8, 113.5, 107.0. IR (KBr, cm $^{-1}$): 3052, 1586, 1510, 1465, 1343, 1211, 1140, 967, 743. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}N_3O_2$ 240.0768, found 240.0766.

Procedure B [22] (**Synthesis of 1i and 1j**): NaH (60% dispersion in mineral oil, 180 mg, 4.5 mmol) was added in portions at 0 ^{o}C to a stirred solution of indole starting material (3.0 mmol) in DMF (10 mL). After stirring for 30 min at 0 ^{o}C, 2-bromopyridine (0.95 g, 6.0 mmol) was added and the mixture was stirred at 110 ^{o}C for 18 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (40 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was extracted with EtOAc (3 × 30 mL), and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents in

vacuo, the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give the desired indole derivatives.

6-Fluoro-1-(pyridin-2-yl)-1H-indole (**1i**): white solid; M. p. = 86–88 °C; 339 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57-8.56 (m, 1H), 8.06 (dd, *J* = 10.8 Hz, 2.1 Hz, 1H), 7.82 (td, *J* = 8.2 Hz, 1.8 Hz, 1H), 7.66 (d, *J* = 3.5 Hz, 1H), 7.55 (dd, *J* = 8.6 Hz, 5.5 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 7.2 Hz, 5.0 Hz, 1H), 6.97 (td, *J* = 9.0 Hz, 2.3 Hz, 1H), 6.68 (d, *J* = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5 (d, *J* = 237.8 Hz), 152.4, 148.9, 138.5, 135.2 (d, *J* = 12.8 Hz), 126.7, 126.0 (d, *J* = 3.8 Hz), 121.5 (d, *J* = 10.1 Hz), 120.2, 114.0, 109.9 (d, *J* = 24.5 Hz), 105.6, 100.6 (d, *J* = 28.2 Hz). IR (KBr, cm^{-1}): 3013, 1699, 1591, 1530, 1462, 1346, 1267, 1206, 930, 756. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}FN_2$ 213.0823, found 213.0822.

6-Chloro-1-(pyridin-2-yl)-1H-indole (**1j**): white solid; M. p. = 110–112 °C; 393 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59-8.57 (m, 1H), 8.33 (m, 1H), 7.83 (td, *J* = 8.2 Hz, 1.9 Hz, 1H), 7.67 (d, *J* = 3.5 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.21-7.16 (m, 2H), 6.68 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2, 148.9, 138.6, 135.5, 129.1, 128.9, 126.4, 121.9, 121.7, 120.4, 114.2, 113.7, 105.6. IR (KBr, cm^{-1}): 3057, 1640, 1520, 1445, 1340, 1266, 1203, 1152, 895, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{13}H_{10}ClN_2$ 229.0527, found 229.0528.

General procedure for the synthesis of the compound 3a-3z, 3za, 3zb, 3zc, 3zd and 3ze

$[RuCl_2(p\text{-cymene})]_2$ (0.007 mmol, 7 mol %), AcOH (0.1 mmol, 1.0 equiv), 1-(Pyridin-2-yl)-1*H*-indole **1a** (0.1 mmol, 1.0 equiv), 1,2-diphenylethyne **2a** (0.2 mmol, 2.0 equiv) were dissolved in 2.0 mL of DMF in a tube, and then the tube was sealed under Ar and heated at 110 °C in an oil bath for 24 h. The reaction progress was monitored by TLC method, after the starting material disappeared; the corresponding reaction mixture was then cooled down and removed the solvent *in vacuum*. The given residue was purified by column chromatography to give **3a**.

(E)-2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3a**): white solid; M. p. = 149–151 °C; 35.0 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44-8.43 (m, 1H), 7.64-7.62 (m, 1H), 7.55 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.42-7.40 (m, 1H), 7.19-7.02 (m, 14H), 6.92 (s, 1H), 6.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.9, 149.1, 142.9, 138.7, 138.6, 137.6, 136.8, 134.2, 130.6, 130.2, 129.5, 128.2, 128.0, 127.9, 127.3, 127.0, 123.1, 121.7, 121.5, 121.1, 120.7, 110.9, 107.4. IR (KBr, cm^{-1}) 3057, 1584, 1454, 1355, 1265, 1208, 1148, 744, 701, 552. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{21}N_2$ 373.1699, found 373.1703.

(E)-2-(1,2-Diphenylvinyl)-5-methoxy-1-(pyridin-2-yl)-1H-indole (**3b**): yellow solid; M. p. = 160–162 °C; 39.0 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43-8.42 (m, 1H), 7.55 (td, *J* = 7.9 Hz, 1.9 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.15-7.00 (m, 13H), 6.88 (s, 1H), 6.83 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.67 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2, 152.0, 149.0, 143.4, 138.6, 137.7 136.8, 134.3, 134.0, 130.6, 130.3, 129.5, 128.8, 128.0, 128.0, 127.4, 127.1, 121.5, 121.4, 113.2, 111.9, 107.5, 102.4, 55.9. IR (KBr, cm^{-1}) 3059, 2924, 2851, 1586, 1462, 1339, 1268, 1215, 1160, 1032, 748. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2O$ 403.1805, found 403.1816.

(E)-2-(1,2-Diphenylvinyl)-5-fluoro-1-(pyridin-2-yl)-1H-indole (**3c**): light yellow solid; M. p. = 158–160 °C; 31.2 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44-8.42 (m, 1H), 7.56 (td, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.35 (dd, *J* = 9.0 Hz, 4.5 Hz, 1H), 7.26 (dd, *J* = 8.7

Hz, 2.9 Hz, 1H), 7.15-7.00 (m, 12H), 6.93-6.88 (m, 2H), 6.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.7 (d, *J* = 235.9 Hz), 151.8, 149.1, 144.5, 138.4, 137.8, 136.7, 135.3, 134.0, 131.3, 130.2, 129.6, 128.7 (d, *J* = 9.9 Hz), 128.1, 127.5, 127.3, 121.8, 121.7, 111.9 (d, *J* = 9.4 Hz), 111.3 (d, *J* = 26.0 Hz), 107.2 (d, *J* = 4.4 Hz), 105.5 (d, *J* = 23.6 Hz). IR (KBr, cm^{-1}) 3058, 1584, 1456, 1266, 1202, 1153, 855, 743. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}FN_2$ 391.1605, found 391.1604.

(E)-5-Chloro-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3d**): light yellow solid; M. p. = 129–131 °C; 38.3 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43-8.42 (m, 1H), 7.59-7.54 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.13-6.98 (m, 13H), 6.92 (s, 1H), 6.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.5, 149.2, 144.2, 138.3, 137.9, 137.1, 136.6, 133.8, 131.4, 130.2, 129.6, 129.3, 128.1, 127.5, 127.3, 126.7, 123.3, 121.9, 121.7, 120.0, 112.2, 106.7. IR (KBr, cm^{-1}) 3056, 1588, 1443, 1370, 1323, 1266, 1207, 1068, 866, 750, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}ClN_2$ 407.1310, found 407.1322.

(E)-5-Bromo-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3e**): light yellow solid; M. p. = 176–178 °C; 42.8 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43-8.42 (m, 1H), 7.75 (d, *J* = 1.4 Hz, 1H), 7.56 (td, *J* = 7.9 Hz, 1.8 Hz, 1H), 7.29-7.23 (m, 2H), 7.13-6.98 (m, 12H), 6.92 (s, 1H), 6.69 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.5, 149.2, 144.1, 138.3, 137.9, 137.3, 136.6, 133.8, 131.4, 130.2, 129.9, 129.6, 128.1, 127.5, 127.3, 125.9, 123.1, 121.9, 121.7, 114.3, 112.6, 106.5. IR (KBr, cm^{-1}) 3058, 1586, 1445, 1369, 1323, 1266, 1207, 750, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}BrN_2$ 451.0804, found 451.0791.

(E)-2-(1,2-Diphenylvinyl)-5-nitro-1-(pyridin-2-yl)-1H-indole (**3f**): yellow solid; M. p. = 187–189 °C; 30.9 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 2.1 Hz, 1H), 8.46-8.44 (m, 1H), 8.07 (dd, *J* = 9.1 Hz, 2.2 Hz, 1H), 7.61 (td, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.16-7.02 (m, 10H), 6.99-6.95 (m, 3H), 6.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.7, 149.4, 146.3, 142.7, 141.2, 138.1, 137.8, 136.1, 133.1, 132.4 130.0, 129.6, 128.2, 128.1, 127.6, 127.6, 127.5, 122.6, 121.8, 118.5, 117.5, 111.0, 107.9. IR (KBr, cm^{-1}) 3058, 1641, 1512, 1464, 1330, 1269, 1071, 743, 700. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}N_3O_2$ 418.1550, found 418.1556.

(E)-2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indole-5-carbonitrile (**3g**): light yellow solid; M. p. = 171–173 °C; 37.3 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45-8.43 (m, 1H), 7.98 (s, 1H), 7.60 (td, *J* = 7.7 Hz, 1.8 Hz, 1H), 7.43-7.38 (m, 2H), 7.14-7.02 (m, 10H), 6.98-6.95 (m, 3H), 6.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.8, 149.3, 145.4, 140.0, 138.1, 137.9, 136.2, 133.2, 132.2, 130.0, 129.6, 128.2, 128.1, 128.0, 127.6, 127.5, 125.9, 122.5, 121.8, 120.5, 111.9, 106.8, 104.2. IR (KBr, cm^{-1}) 3060, 2220, 1580, 1462, 1368, 1327, 1267, 885, 751. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{20}N_3$ 398.1652, found 398.1653.

(E)-Methyl 2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole-5-carboxylate (**3h**): light yellow solid; M. p. = 168–170 °C; 39.1 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44-8.43 (m, 1H), 8.39 (d, *J* = 1.1 Hz, 1H), 7.87 (dd, *J* = 8.7 Hz, 1.5 Hz, 1H), 7.58 (td, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.14-6.96 (m, 13H), 6.85 (s, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.0, 151.3, 149.2, 144.4, 141.0, 138.2, 137.9, 136.5, 133.7, 131.4, 130.1, 129.6, 128.0, 127.8, 127.4, 127.3, 124.4, 123.5, 123.1, 122.1, 121.8, 110.5, 107.8, 51.9. IR (KBr, cm^{-1}) 3058, 2924, 2851, 1710, 1644, 1438, 1310, 1262, 1182, 1133, 1088, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{23}N_2O_2$ 431.1754, found 431.1755.

(E)-2-(1,2-Diphenylvinyl)-6-fluoro-1-(pyridin-2-yl)-1H-indole (**3i**): light yellow solid; M. p. = 88–90 °C; 33.2 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44-8.43 (m, 1H), 7.59-7.51 (m, 2H), 7.17-7.01 (m, 13H), 6.92 (td, *J* = 9.2 Hz, 2.2 Hz, 2H), 6.88 (s, 1H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.7 (d, *J* = 239.2 Hz), 151.7, 149.1, 143.4 (d, *J* = 3.8 Hz), 138.8 (d, *J* = 12.3 Hz), 138.4, 137.9, 136.7, 134.0, 130.7, 130.2, 129.6, 128.1, 127.5, 127.2, 124.7, 121.8, 121.5, 121.4 (d, *J* = 10.3 Hz), 109.8 (d, *J* = 24.5 Hz), 107.4, 97.9 (d, *J* = 27.0 Hz). IR (KBr, cm^{-1}) 3011, 1703, 1579, 1473, 1351, 1268, 755, 702. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}FN_2$ 391.1605, found 391.1605.

(E)-6-Chloro-2-(1,2-diphenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3j**): light yellow solid; M. p. = 143–145 °C; 35.0 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45-8.43 (m, 1H), 7.57 (td, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.14-6.98 (m, 13H), 6.91 (s, 1H), 6.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.4, 149.2, 143.7, 139.0, 138.3, 137.9, 136.6, 133.9, 131.1, 130.2, 129.6, 129.1, 128.1, 127.5, 127.3, 126.8, 121.9, 121.9, 121.6, 121.5, 111.2, 107.2. IR (KBr, cm^{-1}) 3053, 1643, 1451, 1336, 1268, 1206, 818, 754, 699. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{27}H_{20}ClN_2$ 407.1310, found 407.1309.

(E)-2-(1,2-Diphenylvinyl)-7-methyl-1-(pyridin-2-yl)-1H-indole (**3k**): white solid; M. p. = 124–126 °C; 36.3 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35-8.34 (m, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.13-6.86 (m, 15H), 6.74 (s, 1H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.5, 148.3, 144.4, 139.0, 137.7, 136.9, 136.8, 134.4, 131.5, 129.9, 129.6, 128.7, 128.1, 128.0, 127.2, 127.1, 125.6, 125.1, 122.9, 121.7, 120.7, 118.8, 106.1, 19.6. IR (KBr, cm^{-1}) 3059, 2925, 2850, 1588,1471, 1433, 1347, 1266, 1150, 745. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2$ 387.1856, found 387.1856.

(E)-2-(1,2-Diphenylvinyl)-3-methyl-1-(pyridin-2-yl)-1H-indole (**3l**): light yellow solid; M. p. = 136–138 °C; 37.1 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: = 8.38-8.37 (m, 1H), 7.67-7.62 (m, 1H), 7.51 (td, *J* = 7.9 Hz, 1.9 Hz, 1H), 7.45-7.40 (m, 1H), 7.22-7.17 (m, 2H), 7.14-7.11 (m, 6H), 7.01-6.93 (m, 4H), 6.88-6.86 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0, 148.9, 138.8, 138.6, 137.5, 137.2, 137.0, 133.5, 132.7, 130.1, 129.5, 129.5, 128.1, 127.8, 127.1, 123.4, 121.2, 121.1, 120.6, 119.2, 114.5, 110.8, 10.0. IR (KBr, cm^{-1}) 3056, 2922, 2856, 1584, 1459, 1358, 1266, 751, 699. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{28}H_{23}N_2$ 387.1856, found 387.1859.

(E)-1-(2-(1,2-Diphenylvinyl)-1-(pyridin-2-yl)-1H-indol-3-yl)ethanone (**3m**): light yellow solid; M. p. = 176–178 °C; 10.4 mg, 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 8.0 Hz, 1H), 8.36-8.35 (m, 1H), 7.51 (td, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.39-7.33 (m, 3H), 7.30-7.24 (m, 6H), 7.16-7.12 (m, 5H), 7.00-6.98 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.9, 149.9, 149.2, 143.0, 140.5, 137.6, 137.1, 135.9, 134.0, 131.9, 128.8, 128.7, 128.6, 128.4, 128.1, 127.1, 126.7, 124.1, 123.4, 123.1, 122.9, 121.5, 117.7, 111.2, 29.8. IR (KBr, cm^{-1}) 3065, 2923, 2850, 1646, 1574, 1454, 1392, 1179, 757, 689. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{23}N_2O$ 415.1805, found 415.1805.

2-(2,5-Bis((E)-1,2-diphenylvinyl)-1H-pyrrol-1-yl)pyridine (**3n**): yellow solid; M. p. = 191–193 °C; 20.0 mg, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 4.5 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.03-6.96 (m, 12H), 6.91-6.87 (m, 8H), 6.77-6.74 (m, 1H), 6.68 (s, 2H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.35 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.3, 148.3, 139.2, 139.0, 137.2, 136.6, 134.5, 130.0, 129.4,

128.8, 127.8, 127.8, 126.8, 126.5, 123.7, 121.7, 111.8. IR (KBr, cm^{-1}) 3063, 1668, 1534, 1462, 1310, 1277, 1223, 1143, 822, 741. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{37}H_{28}N_2Na$ 523.2145, found 523.2149.

2-(2-((1Z,3E)-1,2,3,4-Tetraphenylbuta-1,3-dienyl)-1H-pyrrol-1-yl)pyridine (**30**): yellow solid; M. p. = 183–185 °C; 26.0 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 4.6 Hz, 1H), 7.28-7.24 (m, 4H), 7.22-7.14 (m, 4H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.04 – 6.99 (m, 9H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.79 (s, 1H), 6.73 – 6.69 (m, 2H), 6.44 (d, *J* = 3.4 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.6, 148.1, 142.2, 139.7, 138.3, 137.6, 137.4, 136.3, 134.4, 133.9, 133.9, 131.1, 130.1, 129.4, 129.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 127.2, 127.0, 126.4, 122.2, 121.3, 112.9, 111.1. IR (KBr, cm^{-1}) 3066, 1671, 1533, 1466, 1302, 1263, 1219, 1139, 810, 744. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{37}H_{28}N_2Na$ 523.2145, found 523.2147.

(E)-2-(1,2-Diphenylvinyl)-1-(pyrimidin-2-yl)-1H-indole (**3p**) [29]: white solid; M. p. = 150–152 °C; 31.0 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 4.8 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.28-7.20 (m, 2H), 7.13-7.10 (m, 7H), 7.04-7.00 (m, 4H), 6.89-6.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.0, 157.6, 142.8, 138.6, 137.9, 137.2, 135.5, 130.5, 129.7, 128.9, 128.0, 127.7, 127.2, 127.0, 123.8, 122.1, 120.7, 117.1, 112.9, 110.1. IR (KBr, cm^{-1}) 3055, 1703, 1545, 1430, 1346, 1264, 744. MS (ESI) m/z 374.2 $[M + H]^+$.

2-(1-Phenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3q**): obtained as a 4:1 mixture with its regioisomer *(E)-1-(pyridin-2-yl)-2-styryl-1H-indole* **3r**; yellow oil; 24.0 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73-8.72 (m, 1H, **3q**), 8.63-8.62 (m, 1H, **3r**), 7.89 (td, *J* = 7.8 Hz, 1.9 Hz, 1H, **3q**), 7.79 (td, *J* = 7.9 Hz, 1.9 Hz, 1H, **3r**), 7.65 – 7.61 (m, 1H, **3q**), 7.57 (d, *J* = 8.3 Hz, 1H, **3r**), 7.51–7.49 (m, 1H, **3q** and **3r**), 7.42 – 7.39 (m, 3H, **3q** and **3r**), 7.36 – 7.29 (m, 3H, **3q** and **3r**), 7.24 – 7.21 (m, 1H, **3q** and **3r**), 7.19 – 7.14 (m, 2H, **3q** and **3r**), 7.10 (d, *J* = 4.4 Hz, 2H, **3q**), 6.98 (s, 1H, **3q**), 6.62 (s, 1H, **3r**), 6.58 (d, *J* = 12.3 Hz, 1H, **3r**), 6.45 (d, *J* = 12.2 Hz, 1H, **3r**). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.4, 151.3, 149.7, 149.3, 138.4, 138.2, 138.0, 137.9, 137.2, 137.2, 137.0, 135.6, 131.8, 130.6, 128.8, 128.7, 128.7, 128.4, 127.8, 127.6, 126.6, 123.0, 123.0, 122.1, 121.6, 121.6, 121.5, 121.2, 121.2, 120.8, 120.6, 120.2, 118.5, 111.3, 111.0, 105.5, 102.4. IR (KBr, cm^{-1}) 3052, 1584, 1463, 1344, 1263, 1213, 1140, 956, 741, 694. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{21}H_{17}N_2$ 297.1386, found 297.1389.

(E)-2-(1-Phenylbut-1-enyl)-1-(pyridin-2-yl)-1H-indole (**3s**): yellow oil; 20.1 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46-8.45 (m, 1H), 7.60-7.56 (m, 2H), 7.41-7.40 (m, 1H), 7.15-7.07 (m, 7H), 7.01-6.99 (m, 2H), 6.62 (s, 1H), 5.98 (t, *J* = 7.4 Hz, 1H), 2.19 (p, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.0, 149.0, 142.7, 138.7, 138.2, 137.6, 135.8, 132.9, 129.7, 128.4, 127.6, 126.9, 122.7, 121.8, 121.5, 121.0, 120.5, 110.9, 106.1, 22.8, 14.4. IR (KBr, cm^{-1}) 3059, 2924, 2856, 1644, 1527, 1457, 1345, 1265, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{21}N_2$ 325.1699, found 325.1699.

(E)-2-(1-Phenylbut-1-en-2-yl)-1-(pyridin-2-yl)-1H-indole (**3t**): yellow oil; 11.0 mg, 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58-8.57 (m, 1H), 7.67 (td, *J* = 7.8 Hz, 1.9 Hz, 1H), 7.57-7.54 (m, 2H), 7.25-7.07 (m, 9H), 6.67 (s, 1H), 6.45 (s, 1H), 2.35 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7, 149.2, 141.8, 138.5, 138.0, 137.4, 136.0, 131.4, 128.6, 128.5, 128.3, 126.8, 123.0 121.7, 121.3, 121.3, 120.4, 111.4, 105.5, 24.2, 13.5. IR (KBr, cm^{-1}) 3054, 2923, 2852, 1638, 1522, 1460, 1342, 1266, 743. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{23}H_{20}N_2Na$ 347.1519, found 347.1521.

(Z)-3-Phenyl-2-(1-(pyridin-2-yl)-1H-indol-2-yl)prop-2-en-1-ol (**3u**): brown solid; M. p. = 78–80 °C; 29.0 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 4.7 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.34-7.30 (m, 2H), 7.28-7.19 (m, 6H), 6.77 (s, 1H), 6.43 (s, 1H), 4.58 (s, 2H), 4.47 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.3, 148.9, 140.8, 138.7, 137.4, 136.2, 134.4, 133.2, 128.9, 128.7, 128.4, 127.6, 123.0, 121.9, 121.5, 121.2, 120.9, 110.6, 105.0, 62.2. IR (KBr, cm^{-1}) 3374, 3058, 2925, 2855, 1705, 1537, 1457, 1346, 1264, 1012, 742. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{22}H_{19}N_2O$ 327.1492, found 327.1492.

(Z)-2-(3-methoxy-1-phenylprop-1-en-2-yl)-1-(pyridin-2-yl)-1H-indole (**3v**): light yellow oil; 26.2 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 4.5 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.33 (dd, *J* = 13.0 Hz, 7.3 Hz, 3H), 7.29–7.13 (m, 6H), 6.85 (s, 1H), 6.63 (s, 1H), 4.18 (s, 2H), 3.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6, 149.1, 140.8, 138.6, 138.0, 136.4, 135.6, 130.0, 128.9, 128.6, 128.3, 127.5, 123.2, 122.0, 121.7, 121.3, 120.7, 111.4, 105.7, 70.7, 58.5. IR (KBr, cm^{-1}) 3053, 2922, 2844, 1569, 1471, 1333, 1260, 1203, 1142, 1014, 741. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{21}N_2O$ 341.1648, found 341.1647.

(E)-Methyl 3-phenyl-3-(1-(pyridin-2-yl)-1H-indol-2-yl)acrylate (**3w**): yellow solid; M. p. = 88–90 °C; 32.9 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48-8.47 (m, 1H), 7.85 (s, 1H), 7.69-7.66 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.31-7.12 (m, 9H), 6.61 (s, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6, 151.3, 149.1, 143.5, 137.8, 136.7, 134.4, 133.5, 130.3, 129.6, 128.7, 128.4, 124.1, 123.1, 121.2, 121.1, 121.1, 119.2, 111.6, 106.7, 52.3. IR (KBr, cm^{-1}) 3057, 2924, 2851, 1713, 1638, 1457, 1382, 1253, 1201, 745, 688. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{19}N_2O_2$ 355.1441, found 355.1442.

(E)-2-(Oct-4-en-4-yl)-1-(pyridin-2-yl)-1H-indole (**3x**): obtained as a 4.2:1 mixture with its stereoisomer *(Z)-2-(oct-4-en-4-yl)-1-(pyridin-2-yl)-1H-indole*; yellow oil; 28.9 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65-8.64 (m, 1H, **3x**(*E*) and **3x**(*Z*)), 7.75 (td, *J* = 7.8 Hz, 1.4 Hz, 1H, **3x**(*E*) and **3x**(*Z*)), 7.58-7.56 (m, 2H, **3x**(*E*) and **3x**(*Z*)), 7.26 – 7.21 (m, 2H, **3x**(*E*) and **3x**(*Z*)), 7.17-7.11 (m, 2H, **3x**(*E*) and **3x**(*Z*)), 6.55 (s, 1H, **3x**(*E*) and **3x**(*Z*)), 5.56 (t, *J* = 7.4 Hz, 1H, **3x**(*E*)), 5.51 (t, *J* = 7.4 Hz, 1H, **3x**(*Z*)), 2.13-2.05 (m, 4H, **3x**(*E*) and **3x**(*Z*)), 1.38-1.26 (m, 4H, **3x**(*E*) and **3x**(*Z*)), 0.91-0.79 (m, 6H, **3x**(*E*) and **3x**(*Z*)). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8, 149.1, 149.1, 142.7, 142.6, 138.1, 137.8, 137.8, 135.1, 133.7, 132.3, 131.7, 128.6, 122.5, 121.5, 121.5, 121.4, 121.0, 120.2, 111.3, 111.2, 104.4, 32.5, 31.0, 30.4, 30.2, 22.7, 21.9, 21.6, 14.1, 14.0, 13.9, 13.9. IR (KBr, cm^{-1}) 3059, 2954, 2863, 1580, 1459, 1348, 1264, 1210, 784, 740. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{21}H_{25}N_2$ 305.2012, found 305.2027.

2-(1-Phenylvinyl)-1-(pyridin-2-yl)-1H-indole (**3q**): obtained as a 19:1 mixture with its regioisomer *(E)-1-(pyridin-2-yl)-2-styryl-1H-indole* **3r**; yellow oil; 29.0 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.6 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.64-7.62 (m, 1H), 7.51-7.49 (m, 1H), 7.42-7.39 (m, 3H), 7.36-7.29 (m, 3H), 7.23-7.15 (m, 3H), 7.11 (s, 1H), 7.09 (s, 1H), 6.98 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.4, 149.7, 138.4, 138.1, 137.9, 137.2, 130.6, 128.8, 128.7, 127.8, 126.6, 123.0, 122.1, 121.6, 121.4, 120.6, 118.4, 111.0, 102.4. IR (KBr, cm^{-1}) 3054, 1582, 1459, 1345, 1267, 1212, 1150, 956, 744, 695. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{21}H_{16}N_2Na$ 319.1206, found 319.1214.

(E)-Ethyl 3-(1-(pyridin-2-yl)-1H-indol-2-yl)acrylate (**3y**): yellow oil; 15.8 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 4.4 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.71-7.65 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.40-7.35 (m, 2H), 7.25-7.16 (m, 2H), 7.12 (s, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 150.6, 149.9, 138.7, 138.6, 134.9, 133.9, 128.1, 124.5, 122.5, 121.8, 121.5, 121.5, 118.6, 111.1, 106.6, 60.5, 14.3. IR (KBr, cm^{-1}) 3051, 2923, 2848, 1717, 1628, 1451, 1388, 1257, 1189, 751. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{18}H_{16}N_2O_2Na$ 315.1104, found 315.1107.

(E)-2-(1-Phenylbuta-1,3-dienyl)-1-(pyridin-2-yl)-1H-indole (**3z**): obtained as a 6.7:1 mixture with its stereoisomer *(Z)-2-(1-phenylbuta-1,3-dienyl)-1-(pyridin-2-yl)-1H-indole*; yellow oil; 26.1 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 4.7 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.70-7.64 (m, 2H), 7.36-7.30 (m, 4H), 7.27-7.14 (m, 5H), 7.07-7.03 (m, 1H), 6.75 (d, *J* = 8.2 Hz, 3H), 5.27 (d, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.3, 149.0, 139.5, 137.8, 137.6, 136.7, 133.6, 133.5, 132.7, 129.5, 128.4, 128.3, 127.5, 123.1, 121.3, 121.3, 120.6, 120.5, 119.8, 111.7, 107.2. IR (KBr, cm^{-1}) 3055, 1592, 1466, 1353, 1255, 1218, 1144, 742. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{23}H_{18}N_2Na$ 345.1362, found 345.1369.

(E)-2-(1,4-Diphenylbut-1-en-3-ynyl)-1-(pyridin-2-yl)-1H-indole (**3za**): brown oil; 34.8 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 4.4 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 14.0 Hz, 7.5 Hz, 3H), 7.36-7.22 (m, 9H), 7.13 (s, 1H), 6.96 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2, 149.3, 139.6, 138.5, 138.0, 137.3, 136.3, 131.4, 129.1, 128.7, 128.5, 128.4, 128.3, 128.2, 123.4, 122.9, 121.8, 121.5, 121.4, 120.8, 113.9, 111.3, 106.0, 97.3, 87.7. IR (KBr, cm^{-1}) 3058, 2196, 1641, 1456, 1363, 1264, 1208, 1150, 743, 688. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{29}H_{21}N_2$ 397.1699, found 397.1697.

2-Heptyl-1-(pyridin-2-yl)-1H-indole (**3zb**): Obtained as a 6.7:1 mixture with its regioisomer *2-(heptan-2-yl)-1-(pyridin-2-yl)-1H-indole* (**3zc**); yellow oil; 22.2 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 4.7 Hz, 1H, **3zb** and **3zc**), 7.73 (t, *J* = 7.7 Hz, 1H, **3zb** and **3zc**), 7.55-7.53 (m, 1H, **3zb** and **3zc**), 7.34-7.28 (m, 2H, **3zb** and **3zc**), 7.20-7.17 (m, 1H, **3zb** and **3zc**), 7.11-7.08 (m, 2H, **3zb** and **3zc**), 6.44 (s, 1H, **3zc**), 6.42 (s, 1H, **3zb**), 3.22-3.13 (m, 1H, **3zc**), 2.81 (t, *J* = 7.7 Hz, 2H, **3zb**), 1.57-1.50 (m, 2H, **3zb** and **3zc**), 1.26-1.20 (m, 8H, **3zb**; 6H, **3zc**), 0.86-0.77 (m, 3H, **3zb**; 6H, **3zc**). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.7, 149.7, 141.9, 138.3, 137.4, 128.8, 122.1, 121.6, 121.2, 120.6, 119.9, 110.1, 102.1, 31.8, 29.3, 29.1, 28.7, 27.5, 22.7, 14.2. IR (KBr, cm^{-1}) 3055, 2936, 2845, 1582, 1461, 1345, 1246, 1216, 743. HRMS (ESI-TOF) calcd for $[M+H]^+$ $C_{20}H_{25}N_2^+$ 293.2012, found 293.1995.

(E)-2-(hept-1-enyl)-1-(pyridin-2-yl)-1H-indole (**3zd**): obtained as a 2.3:1 mixture with its regioisomer *2-(hept-1-en-2-yl)-1-(pyridin-2-yl)-1H-indole* (**3ze**); yellow oil; 24.9 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H, **3zd** and **3ze**), 7.77-7.71 (m, 1H, **3zd** and **3ze**), 7.62-7.50 (m, 1H, **3zd**; 2H, **3ze**), 7.45-7.44 (m, 1H, **3zd**), 7.30-7.26 (m, 1H, **3zd** and **3ze**), 7.23-7.10 (m, 3H, **3zd** and **3ze**), 6.73 (s, 1H, **3zd**), 6.69 (s, 1H, **3ze**), 6.32 (d, *J* = 15.9 Hz, 1H, **3zd**), 6.25-6.18 (m, 1H, **3zd** and **3ze**), 5.76-5.70 (m, 1H, **3ze**), 2.47 (dd, *J* = 14.1 Hz, 7.0 Hz, 2H, **3ze**), 2.14 (dd, *J* = 13.8 Hz, 6.8 Hz, 2H, **3zd**), 1.51-1.28 (m, 6H, **3zd** and **3ze**), 0.91-0.86 (m, 3H, **3zd** and **3ze**). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.5, 149.5, 149.5, 138.5, 138.1, 138.1, 137.5, 136.9, 136.0, 135.2, 134.2, 128.8, 128.8, 122.8, 122.4, 121.9, 121.9, 121.6, 121.6, 121.2, 121.1, 120.5, 120.2, 120.0, 118.9, 111.2, 110.9, 105.3, 101.3, 33.3, 31.8, 31.5, 29.6, 29.4, 28.9, 22.7, 22.6, 14.2. IR

(KBr, cm^{-1}) 3066, 2955, 2867, 1592, 1463, 1336, 1258, 1203, 962, 887, 744. HRMS (ESI-TOF) calcd for $[M + Na]^+$ $C_{20}H_{22}N_2Na$ 313.1675, found 313.1678.

Several examples about removal of the pyridyl group of 3

Methyl trifluoromethanesulfonate (0.36 mmol, 1.2 eq.) was added dropwise to a solution of **3** (0.30 mmol, 1.0 eq.) in CH_2Cl_2 (7.5 mL) at 0 °C, and the resulting solution was stirred for 24 h at room temperature. Then the solvent was removed under vacuum, and the residue was dissolved in MeOH (3.6 mL). A 2M aq NaOH solution (1.8 mL) was added, and stirring was continued at 60 °C for 12 h. The solvents were removed, and the resulting residue was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography to afford **4**.

(E)-2-(1, 2-Diphenylvinyl)-1H-indole (**4a**) [29, 30]: light yellow solid; M. p. = 137–139 °C; 80.0 mg, 90.4% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.41-7.40 (m, 3H), 7.35-7.34 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.17-7.06 (m, 6H), 7.01-6.99 (m, 2H), 6.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.2, 138.4, 136.7, 136.6, 134.0, 130.2, 129.6, 129.0, 128.9, 128.2, 128.2, 127.1, 125.9, 122.7, 120.7, 120.3, 110.8, 103.1. IR (KBr, cm^{-1}) 3455, 3096, 1622, 1489, 1332, 1251, 1201, 1143, 741. MS (ESI) m/z 296.1 $[M + H]^+$.

(E)-2-(1,2-diphenylvinyl)-5-methoxy-1H-indole (**4b**) [31]: brown solid; M. p. = 142–145 °C; 80.3 mg, 82.4% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.39 (m, 3H), 7.33 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.12-7.07 (m, 3H), 7.04 (s, 1H), 7.00-6.98 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.37 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: = 154.4, 140.9, 138.3, 136.6, 134.0, 131.9, 130.2, 129.5, 129.3, 129.0, 128.1, 128.1, 127.0, 125.7, 113.0, 111.5, 102.6, 102.2, 55.8. IR (KBr, cm^{-1}) 3458, 3098, 2934, 2862, 1618, 1493, 1335, 1266, 1210, 1163, 744. MS (ESI) m/z 326.2 $[M + H]^+$.

(E)-5-bromo-2-(1,2-diphenylvinyl)-1H-indole (**4c**): yellow solid; M. p. = 161–163 °C; 96.8 mg, 86.3% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.64 (s, 1H), 7.42-7.41 (m, 3H), 7.33 (m, 2H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.15-7.12 (m, 4H), 7.08 (s, 1H), 7.01-6.99 (m, 2H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.4, 138.0, 136.2, 135.2, 133.4, 130.6, 130.1, 129.5, 129.1, 128.3, 128.2, 127.3, 126.8, 125.3, 123.0, 113.3, 112.1, 101.9. IR (KBr, cm^{-1}) 3453, 3091, 1621, 1493, 1340, 1256, 1201, 1138, 742, 698. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{22}H_{17}BrN^+$ 374.0539, found 374.0514.

(E)-2-(1,2-diphenylvinyl)-3-methyl-1H-indole (**4d**): light yellow solid; M. p. = 120–122 °C; 79.7 mg, 86.0 % yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.33 (m, 3H), 7.28 (m, 2H), 7.21-7.05 (m, 8H), 6.91 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 136.9, 135.6, 135.4, 134.4, 130.3, 129.9, 129.6, 129.5, 128.9, 128.1, 128.0, 126.9, 122.6, 119.4, 118.9, 110.8, 110.6, 10.2. IR (KBr, cm^{-1}) 3457, 3098, 2925, 2854, 1624, 1493, 1338, 1243, 1155, 746. HRMS (ESI-TOF) calcd for $[M + H]^+$ $C_{23}H_{20}N^+$ 310.1590, found 310.1587.

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Notes

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Supporting Information

Details for experiments conditions, copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds, and single crystal data of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Graphic Abstract